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Crystal structure of 4-chloro-<i>N</i>′-[(1<i>E</i>)-(2-nitrophenyl)methylidene]benzohydrazide, C₁₄H₁₀ClN₃O₃

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Crystal structure of 4-chloro-*N′*-[(1*E*)-(2-nitrophenyl)methylidene]benzohydrazide, $C_{14}H_{10}ClN_3O_3$

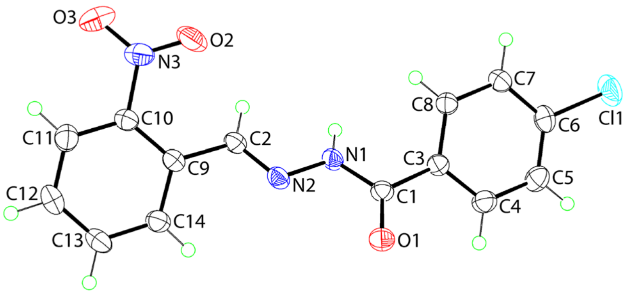

Table 1: Data collection and handling.

Crystal:	Colourless plate
Size:	0.19 × 0.09 × 0.03 mm
Wavelength:	Cu *Kα* radiation (1.54184 Å)
μ:	2.68 mm^{-1}
Diffractometer, scan mode:	XtaLAB Synergy,
θ_{max}, completeness:	74.4°, >99 %
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	6795, 2120, 0.020
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 2092
$N(param)_{refined}$:	193
Programs:	CrysAlis^{PRO} [1], SHELX [2, 3], WinGX/ORTEP [4]

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Abstract
$C_{14}H_{10}ClN_3O_3$, triclinic, $P1$ (no. 1), a = 4.8813(2) Å, b = 6.7806(2) Å, c = 10.3135(2) Å, α = 98.101(2)°, β = 94.174(2)°, γ = 97.612(3)°, V = 333.515(18) Å^3, Z = 1, $R_{gt}(F)$ = 0.0270, $wR_{ref}(F^2)$ = 0.0743, T = 160 K.

CCDC no.: 2245655

The molecular structure is shown in the figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

1 Source of material

A mixture of 4-chlorobenzohydrazide (0.85 g, 5.0 mmol) and 2-nitrobenzaldehyde (0.76 g, 5.0 mmol), in ethanol (8 mL), was heated under reflux for 2 h. On cooling, the precipitated crude product was filtered, washed with cold ethanol, dried and recrystallised from ethanol to yield 1.29 g (85 %) of (I) as colourless plates. Melting point: 499–501 K (uncorrected). ^{1}H NMR (DMSO-d_6, 500.13 MHz): δ 11.55 (s, 1H, NH), 8.85 (s, 1H, CH=N), 8.09 (d, 1H, Ar–H, J = 6.8 Hz), 7.92–7.96 (m, 3H, Ar–H) and 7.55–7.69 (m, 4H, Ar–H). ^{13}C NMR (DMSO-d_6, 125.76 MHz): δ 166.24 (C=O), 143.68 (CH=N), 146.30, 138.20, 134.0, 132.82, 131.94, 130.89, 129.89, 128.24, 127.98, 123.54 (Ar–C). Analysis (%) for $C_{14}H_{10}ClN_3O_3$ (303.70): C, 55.35 (Calc. 55.37); H, 3.36 (Calc. 3.32); N, 13.68 (Calc. 13.84).

2 Experimental details

The C-bound H atoms were geometrically placed (C–H = 0.95 Å) and refined as riding with U_{iso} (H) = 1.2U_{eq}(C). The N-bound H atoms were located in a difference map and refined with N–H = 0.88 ± 0.01 and with U_{iso}(H) = 1.2U_{eq}(N).

3 Comment

N′-Arylidene hydrazide derivatives have been utilised as important starting materials in the synthesis of various heterocyclic compounds having diverse biological activities [5–8]. Herein, the crystal and molecular structures of the title *N′*-arylidene hydrazide derivative, (I), are described,

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Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2).

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
Cl1	0.77208 (13)	1.39448 (9)	0.90495 (7)	0.0486 (2)
O1	0.0578 (3)	0.5145 (2)	0.61964 (18)	0.0352 (4)
O2	0.8047 (5)	0.2378 (3)	0.2036 (2)	0.0578 (6)
O3	0.9425 (4)	−0.0212 (3)	0.0955 (2)	0.0492 (5)
N1	0.4826 (3)	0.4567 (3)	0.56303 (19)	0.0268 (4)
H1N	0.663 (3)	0.492 (4)	0.582 (3)	0.032*
N2	0.3741 (3)	0.2800 (3)	0.48170 (19)	0.0270 (4)
N3	0.7928 (4)	0.0562 (3)	0.1714 (2)	0.0358 (4)
C1	0.3092 (4)	0.5688 (3)	0.6255 (2)	0.0255 (4)
C2	0.5537 (4)	0.1909 (3)	0.4213 (2)	0.0260 (4)
H2	0.743183	0.249572	0.429985	0.031*
C3	0.4399 (4)	0.7672 (3)	0.6998 (2)	0.0245 (4)
C4	0.3191 (4)	0.8517 (4)	0.8089 (2)	0.0313 (5)
H4	0.164580	0.776910	0.839375	0.038*
C5	0.4216 (5)	1.0430 (4)	0.8733 (2)	0.0348 (5)
H5	0.340023	1.098837	0.948294	0.042*
C6	0.6444 (5)	1.1525 (3)	0.8273 (2)	0.0320 (5)
C7	0.7701 (4)	1.0723 (3)	0.7187 (2)	0.0292 (5)
H7	0.923578	1.148343	0.688332	0.035*
C8	0.6676 (4)	0.8804 (3)	0.6561 (2)	0.0274 (4)
H8	0.752389	0.823948	0.582365	0.033*
C9	0.4603 (4)	−0.0045 (3)	0.3380 (2)	0.0253 (4)
C10	0.5801 (4)	−0.0767 (3)	0.2249 (2)	0.0278 (4)
C11	0.5018 (5)	−0.2679 (4)	0.1555 (2)	0.0349 (5)
H11	0.590042	−0.311465	0.079621	0.042*
C12	0.2921 (6)	−0.3956 (4)	0.1983 (3)	0.0386 (5)
H12	0.236011	−0.527847	0.151982	0.046*
C13	0.1659 (5)	−0.3291 (4)	0.3082 (3)	0.0343 (5)
H13	0.020480	−0.415671	0.336644	0.041*
C14	0.2485 (4)	−0.1375 (3)	0.3779 (2)	0.0299 (5)
H14	0.160278	−0.095539	0.454084	0.036*

complemented with an analysis of the calculated Hirshfeld surfaces and a comparison with the isomorphous bromo derivative [9].

The molecular structure of (I) is shown in the figure (50% probability ellipsoids). The central residue, comprising the C1, C2, N1, N2 and O1 atoms is close to planar, exhibiting an r.m.s. deviation of 0.0180 Å; the maximum deviations from the least-squares plane through these atoms are C1 [0.0237(14) Å] and N1 [0.0247(14) Å] atoms which lie to opposite sides of the plane. Each of the attached chlorophenyl and nitrophenyl rings is rotated out of the plane through the central residue, forming dihedral angles of 32.54(11) and 36.61(11)°, respectively. A disrotatory relationship exists between the phenyl rings as indicated by the dihedral angle between them of 4.08(15)°. The nitro group is twisted out of the plane through the ring to which it is connected, forming a dihedral angle of 20.9(3)°. The constituent atoms of the amide group adopt an trans-conformation, and the configuration about the C2=N2 imine bond [1.279(3) Å] is *E*.

In the crystallographic literature, there is the isostructural bromo derivative [9], (II), along with the parent nitro compound [10], (III), available for comparison; the parent nitro compound is not a hydrate as indicated in the title of the publication [10]. An overlay diagram (not shown) of (I)-(III) shows (I) and (II) to be virtually superimposable. However, minor differences are evident for (III), most notably in the opposite orientation of the nitro group; the dihedral angles between the outer rings in (II) and (III) are 4.13(9) and 1.45(8)°, respectively, *cf.* 4.08(15)° for (I).

In the molecular packing, amide-N–H···O(amide) hydrogen bonds feature in linear chains along the *a*-axis [N1–H1n···O1^i: H1n···O1^i = 1.920(16) Å, N1···O1^i = 2.790(2) Å with angle at H1n = 169(3)° for symmetry operation (i): $1 + x, y, z$]. Connections between chains are of the type nitrophenyl-C–H···Cl [C11–H11···Cl1^{ii}: H11···Cl1^{ii} = 2.77 Å, C11···Cl1^{ii} = 3.645(2) Å with angle at H11 = 153° for (ii): $x, -2 + y, -1 + z$]. Bifurcated nitrophenyl-C–H···O(nitro) interactions occur along the b-axis [C12–H12···O2^{iii}: H12···O2^{iii} = 2.60 Å, C12···O2^{iii} = 3.215(4) Å with angle at H12 = 123° and C12–H13···O2^{iii}: H13···O2^{iii} = 2.60 Å, C12···O2^{iii} = 3.218(3) Å with angle at H13 = 123° for (iii): $-1 + x, -1 + y, z$] whereby the nitro atom forms two weak contacts with adjacent hydrogen atoms on the nitrophenyl ring.

An analysis of the calculated Hirshfeld surfaces for (I) and isostructural (II) were also conducted employing CrystalExplorer [11] following literature precedents [12]. This analysis on the packing in the crystal of (I) indicates a wide range of significant surface contacts with 83.5 % of these involving hydrogen. Thus, in descending order of significance, O···H/H···O contacts contributed 25.0 % of all contacts followed by H···H [19.7 %], C···H/H···C [19.5 %], Cl···H/H···Cl [13.6 %] and N···H/H···N [5.7 %]. Significant contributions were also made by O···C/C···O [6.1 %] and N···C/C···N [4.1 %] contacts, with smaller contributions from C···C [2.0 %], Cl···O/O···Cl [2.0 %] and Cl···C/C···Cl [1.6 %] contacts. The comparable analysis performed for (II) revealed differences of equal to or less than 0.4 % to smaller values for all contacts with the notable exception being a plus 1.3 % increase for Br···H/H···Br contacts, an observation consistent with the larger size of the halide atom in (II); a 0.3 % increase for O···H/H···O contacts is also noted.

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Conflict of interest statement: The authors declare no conflicts of interest regarding this article.

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